

Near-IR Photoluminescence of C_{60}^+ and Implications for Astronomy

Dmitry Strelnikov,^{*} Bastian Kern,[†] and Manfred M. Kappes

Karlsruhe Institute of Technology (KIT),

Division of Physical Chemistry of Microscopic Systems, Karlsruhe, Germany

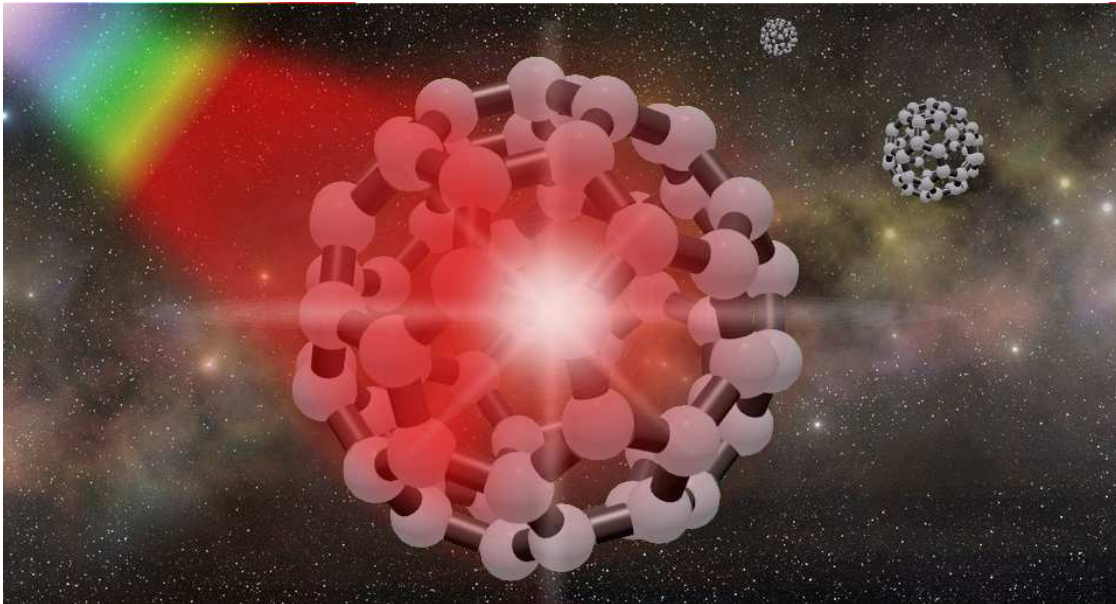
(Dated: April 6, 2017)

Abstract

We have observed that C_{60}^+ ions isolated in cryogenic matrixes show pronounced near-IR photoluminescence upon excitation in the near-IR range. By contrast UV photoexcitation does not lead to measurable luminescence. After the recent unequivocal assignment of five Diffuse Interstellar Bands to near-IR absorption bands of C_{60}^+ , we propose to search also for C_{60}^+ near-IR emission in those astronomical objects, where fullerenes have been already detected or may be potentially present.

^{*} dmitry.strelnikov@kit.edu

[†] current address: Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany



TOC Figure: C_{60}^+ strongly emits Stokes-shifted near-IR photons after near-IR excitation. The schematic drawing indicates a probable scenario in which the UV component of the excitation light is scattered away by dust particles.

Recently, there has been renewed interest in fullerenes in several research fields including astronomy, astrophysics, physical chemistry and quantum chemistry. This was triggered by the detection of the neutral forms of C_{60} and C_{70} in circumstellar environments[1–4] and of charged C_{60}^+ in the diffuse interstellar medium[5, 6]. The firm identification of C_{60} and C_{70} was based on their vibrational infrared emissions, while C_{60}^+ was identified by its electronic absorptions in the near-IR region. As a corollary, C_{60}^+ has turned out to be responsible for several of the known but previously unassigned diffuse interstellar bands (DIBs)[7]. Thus a first significant step towards solving an almost 100 years old puzzle in the spectroscopical and astronomical communities has now been taken. There are also hints for the presence of $C_{60}^{+/2+}$ in the circumstellar environments, based on the infrared spectral data[8, 9].

Most of the UV-vis and near-IR region spectral bands observed in circumstellar environments are absorption features. The light source in this case is simply

the star behind the clouds, containing the absorbing molecules. On the other hand, most of the corresponding astronomical spectral features observed in the mid-IR region are emission bands. Molecular-like emission in the shorter wavelength range of electronic transitions is not a frequently observed phenomenon in astronomy. There are exceptions: one of the most prominent objects, having emission lines in the visible range is the 'Red Rectangle' nebula in the Monoceros constellation[10].

In our laboratory investigation of fullerene ions, we found that C_{60}^+ manifests pronounced fluorescence in the near-IR, when also photo-excited in the near-IR. We suggest therefore to look for the characteristic near-IR emission features of C_{60}^+ in astronomical environments, where either C_{60}/C_{60}^+ has already been detected or where fullerenes are likely to be present. Below we provide the first quantitative experimental data characterizing this emission.

Fig. 1a shows three spectroscopic measurements carried out on the same sample, containing known concentrations of C_{60}^+ , C_{60}^- and C_{60} isolated in a Ne matrix at 5 K: (i) a transmission spectrum, (ii) a laser-induced dispersed fluorescence (LIF) spectrum obtained upon excitation at 785 nm and (iii) a corresponding LIF measurement upon laser excitation at 405 nm. LIF measurement (ii) shows an emission band at 965 nm which is Stokes shifted by about 1.3 nm from the 0-0 transition of C_{60}^+ in neon. This band can be observed only in samples, containing C_{60}^+ . One can also recognize a LIF transition to the first vibrationally excited level of the electronic ground state shifted by about 25 nm (262 cm^{-1}) to lower energies. This fits to a radial vibrational mode of C_{60}^+ – probably, the quadrupolar deformation mode A_{1g} calculated to lie at 258 cm^{-1} for the isolated molecule (harmonic frequency, RI-DFT BP86/def-SV(P) level of theory)[11]. Laser excitation at shorter wavelengths in the UV region (405 nm and also 375 nm (not shown)) does not lead to detectable emission at 965 nm. Instead we observe a weak featureless emission slowly increasing into the IR. The carrier of the latter is unclear. It is however only observed for fullerene containing matrixes and may reflect multiphoton absorption processes. While matrix isolated C_{60} is known to show broad weak photoluminescence upon UV excitation[12–14], there have been

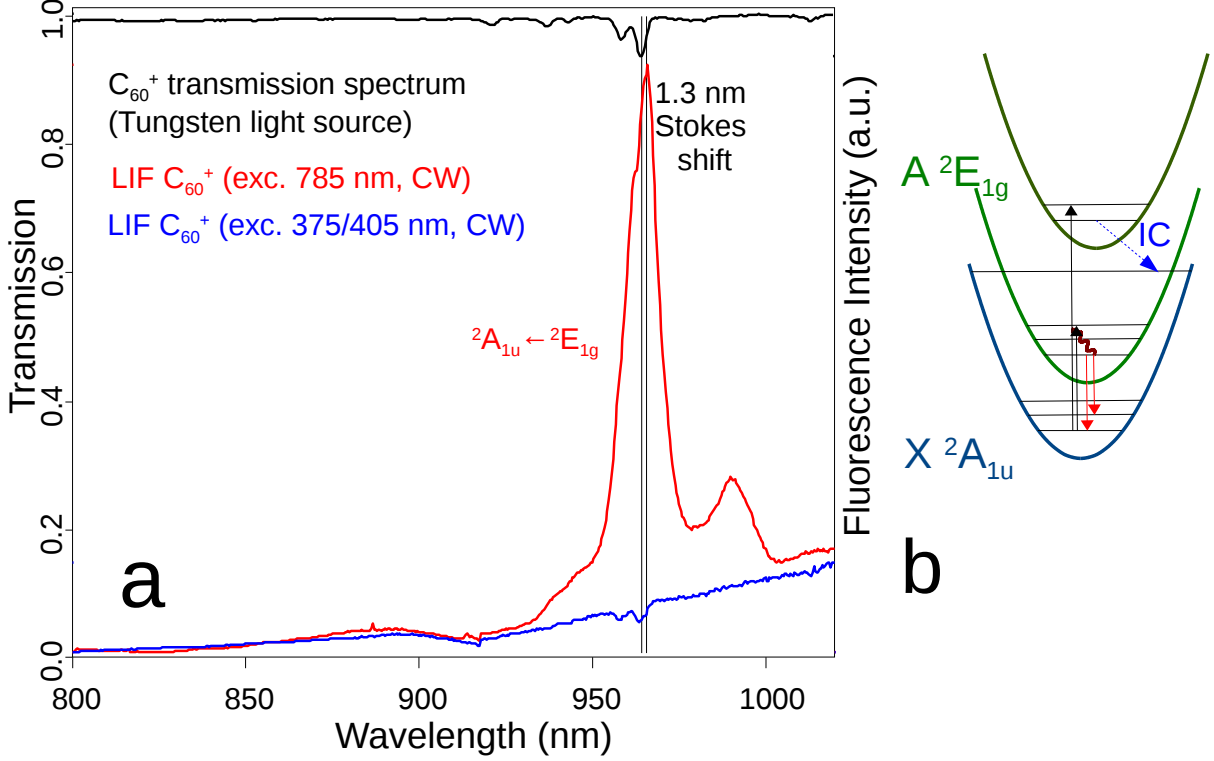


FIG. 1: (a) Spectroscopic measurements on C_{60}^+ containing cryogenic neon matrixes as indicated. (b) Energy level diagram rationalizing these observations in terms of radiative (red arrows) and non-radiative decays.

no previous reports of light emission from C_{60}^+ .

To confirm that the 965 nm emission really originates from C_{60}^+ , we also used tunable pulsed laser excitation from 800 nm to 940 nm in order to record a photoluminescence excitation spectrum – this wavelength region contains the known electronic absorptions ${}^2E_{1g} \leftarrow X^2A_{1u}$ of C_{60}^+ [9, 15, 16]. The corresponding photoluminescence map is displayed in Fig. 2a. A comparison of the photoluminescence excitation and absorption spectrum is shown in Fig. 2b. For the excitation spectrum the integrated intensity of the 965 nm band was used as an ordinate. It is apparent, that the spectra are very similar and therefore that the 965 nm emission band is produced by C_{60}^+ upon population of its first excited state.

We also checked the laser power dependence of the 965 nm emission band intensity. This measurement revealed a one photon process. We have also determined an upper limit for the lifetime of the excited state to be 2 ns. The fluorescence quantum yield for C_{60}^+ absorptions in the range [775; 971] nm was estimated to be $\Phi \gtrsim 4.2 \cdot 10^{-4}$. All these measurements are detailed in Supporting Information.

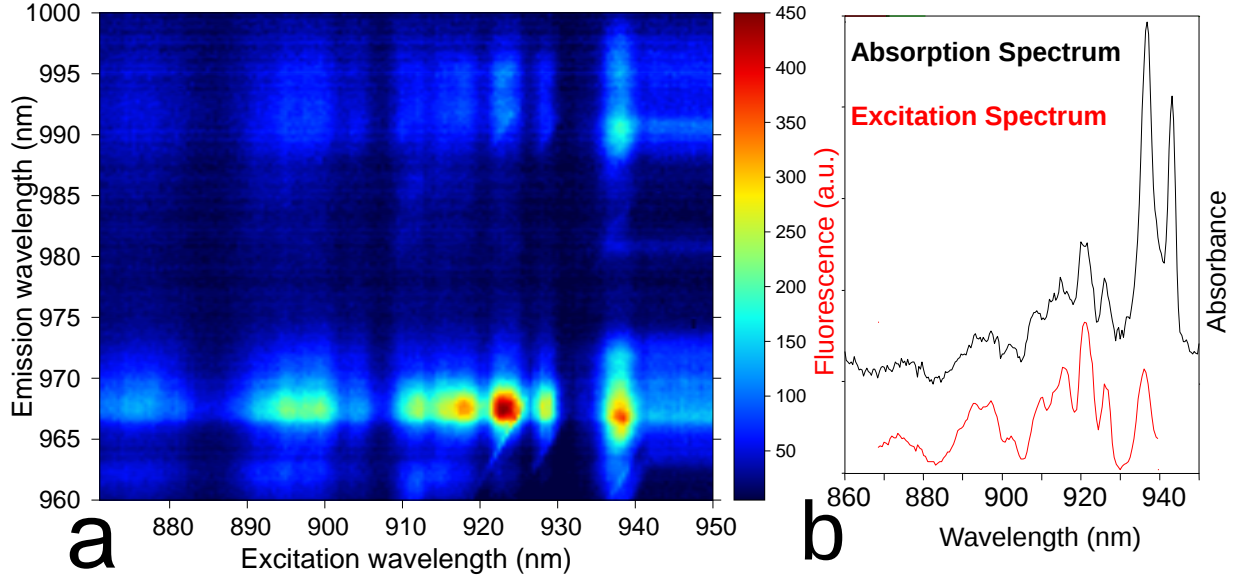


FIG. 2: **(a)** Fluorescence excitation/emission map obtained by tunable pulsed laser irradiation of a C_{60}^+ containing neon matrix. **(b)** Fluorescence excitation spectrum (integrated emission as a function of excitation wavelength) in comparison to the absorption spectrum of C_{60}^+ .

From the astronomical point of view it is important to know the gas-phase position of this emission. The 0-0 electronic absorption transition of C_{60}^+ has been found to lie at 963.2 nm in gas phase[5]. Assuming, that the Stokes shift is similar to that in the Ne-matrix environment, we predict the position of the gas-phase emission maximum to be 964.5 nm. Regarding the line width, it is most likely similar to the absorption line width which was found to be 2–3 Å for isolated C_{60}^+ held in an 4 K ion trap[5]. Neutral diffuse clouds and molecular clouds potentially containing C_{60}^+ can have temperatures in the range 10–100 K. Therefore we also explored the temperature dependence of C_{60}^+ fluorescence by performing analogous measurements in Kr matrix. These measurements at various temperatures up to 50 K revealed no significant changes of LIF intensity (below 7%). By extrapolation we expect that C_{60}^+ still measurably photoluminesces in the near-IR at temperatures up to 100 K.

Taking into account all experimental information (position, linewidth, NIR single-photon excitation, quantum efficiency) we propose to search for the C_{60}^+ emission in those astronomical objects, for which C_{60}/C_{60}^+ has already been detected. Particularly promising from this

point of view would be those objects in which only NIR excitation can take place (simultaneous UV excitation would produce additional background from fullerenes and other species present, thus decreasing the contrast and making detection of the C_{60}^+ NIR emission signal more difficult). One of the candidate objects could be the reflection nebula *CED 201*, where neutral C_{60} has been already detected [17]. This object shows unidentified luminescence bands in the visible range (465–752 nm)[18], which may possibly extend into the near-IR.

METHODS

Sample preparation

The UHV experimental setup for optical spectroscopy of mass-selected species has already been described in our previous publications[9, 19, 20]. Briefly, C_{60}^+ ions are produced in an electron-impact ionization source, guided through an electrostatic lens system, mass selected by a quadrupole mass filter and co-deposited with neon or other rare gases onto a 5 K Al- or Au-coated sapphire substrate. The ion current of mass-selected C_{60}^+ is usually 150-250 nA. Despite our only depositing C_{60}^+ , the matrix formed also contains C_{60} and C_{60}^- which are generated by neutralization and charge changing processes during soft landing of the cations. Under typical deposition conditions the resulting matrixes contain an approximate ratio of $(20\%C_{60}^+)/((60\%C_{60})/(20\%C_{60}^-))$ [19]. For the measurements described we deposited about 10^{14} C_{60}^+ ions.

LIF Spectroscopy

For photoexcitation we used CW diode lasers at 375, 405, 785 nm as well as a 10 ns pulse width OPO laser running at a repetition rate of 20 Hz (and tunable in the 870–950 nm range (idler beam of a Coherent Panther OPO laser)). The sample spot diameter was about 10 mm. The laser beam diameters at sample were about 1 mm for the 375, 405 and the OPO lasers and 100 μ m for the 785 nm laser. Typical irradiation powers were: 20 mW for the 375 nm laser, 20–200 mW for the 405 nm laser, 10-250 mW for the 785 nm laser, and about 1 mW for the pulsed laser. A 950 nm shortpass filter was used to clean up the tunable pulsed laser excitation light. A Raman spectrometer (Kaiser Optics RXN1) with a 950 nm

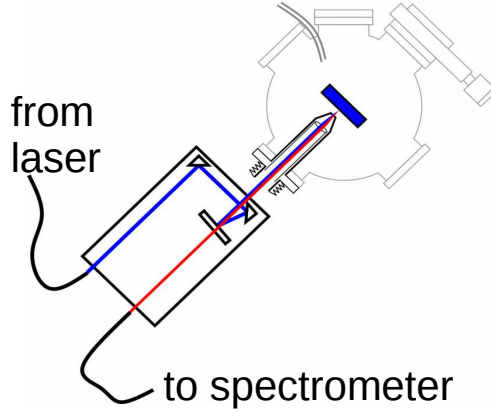


FIG. 3: Experimental configuration for fluorescence measurements of C_{60}^+ in neon.

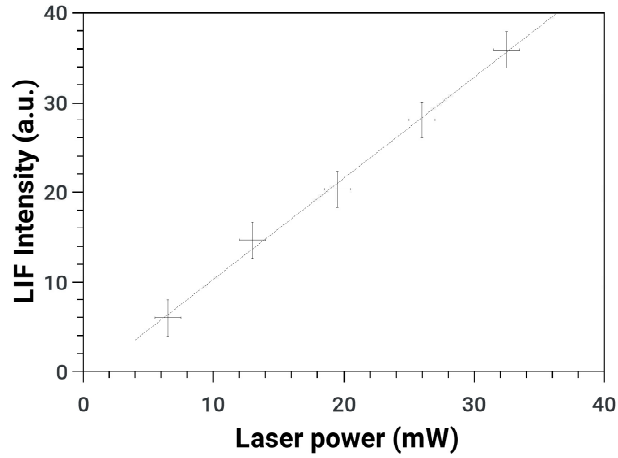


FIG. 4: Total fluorescence intensity versus laser power (785 nm excitation).

longpass filter (Thorlabs FELH0950) was used to detect the emission. The corresponding excitation and collection geometry was perpendicular to the substrate, Fig. 3.

Power dependence

Power dependence measurements were performed using the 785 nm CW diode laser. We found that the matrix samples start to degrade upon excitation with more than 150 mW of laser power. Below this power level LIF signal intensity remains reproducible when switching back and forth between different excitation powers. For excitation powers below 40 mW, the LIF intensity clearly showed a linear dependence, Fig. 4, indicating a one-photon process.

Quantum efficiency

To estimate the quantum efficiency of the C_{60}^+ NIR emission, one has to know the number of excitation photons, the C_{60}^+ quantity and absorption cross section at the excitation wavelength – as well as the corresponding number of emitted photons.

The accuracy to which some of these quantities can be determined is limited by instrumental factors which can be best taken into account by applying a reference standard. As a reference substance we took benzene. Its non-resonant Raman cross-section for an excitation at 785 nm can be extrapolated from experimental data[21]: $(\frac{d\sigma}{d\Omega})_{benzene} \approx 5 \cdot 10^{-30} [cm^2 Molec^{-1} Sr^{-1}]$ for the 992 cm^{-1} Raman line. The Raman cross-section is defined as $\frac{d\sigma}{d\Omega} = P_R/I_{ex}$, where P_R is the power of the Raman emission and $I_{ex} [W \cdot cm^{-2}]$ is the power density of the excitation light. The specifications of the Raman MKII Probe Head with NCO-1.3-VIS/NIR optics are as follows: the collection zone diameter is $d = 100 \mu m$, the collection zone depth is $l = 500 \mu m$, and the light-collection solid angle of the objective is $\Omega \approx 0.2$ Sr. We accumulated Raman emission of benzene for $\Delta t = 1$ s, exciting with the $P_{ex} = 1$ mW CW laser at $\lambda_{ex} = 785$ nm. The total number of emitted photons collected by the objective is then

$$N_{photons} = \frac{d\sigma}{d\Omega} \Omega \frac{P_{ex}}{\pi(\frac{d}{2})^2} \Delta t \frac{\lambda_{ex}}{hc} N_{molecules},$$

where $N_{molecules}$ is the number of benzene molecules in the collection volume. For the listed parameters this corresponds to $N_{photons} \approx 1.5 \cdot 10^6$ for the benzene 992 cm^{-1} Raman line. This number of photons corresponds to 1730 intensity counts at 851 nm (992 cm^{-1} Raman shift) as registered by the CCD detector and displayed by the spectrometer software.

We deposited about 5000 nA·min of C_{60}^+ to create a neon matrix, containing $C_{60}^{+/-/0}$. From our previous experiments, we know that the charge distribution is roughly 20:20:60 for +/-/0 respectively. Therefore, the amount of C_{60}^+ is about $3.75 \cdot 10^{14}$ ions. These ions are almost homogeneously distributed over a spot about 10 mm in diameter (as experimentally determined). Correspondingly, the number of C_{60}^+ ions in the Raman signal collection zone is (100 μm diameter) about $3.75 \cdot 10^{10}$. Exciting this amount of C_{60}^+ with a 1 mW laser and accumulating for 1 s gives rise to $7.5 \cdot 10^3$ (intensity corrected, because the reference substance emission is at 851 nm, where the CCD has larger sensitivity) intensity counts or $3.2 \cdot 10^6$ photons of C_{60}^+ emission. The total number of emitted photons in all directions would be about $2 \cdot 10^8$ corresponding to the 1 mW excitation/1 s accumulation parameters.

The number of the absorbed photons at wavelength λ can be derived using the Lambert-Beer law and relations between oscillator strength f_λ and absorption cross section at this wavelength[22]:

$$N_{absPh} = N_{exPh} \left(1 - \exp \left(- \frac{e^2}{\varepsilon_0 m_e c \Delta\omega_\lambda} f_\lambda \frac{N_{C60+}}{\pi (d/2)^2} \right) \right),$$

where $\Delta\omega_\lambda$ (rad/s) is the fwhm of the absorption at the wavelength λ .

The oscillator strength of the C_{60}^+ absorption at 785 nm is hard to estimate, because it can not be clearly distinguished from the noise at this wavelength, therefore we set only an upper limit: $f_{785} \leq 2 \cdot 10^{-5}$. In this wavelength range, stronger and therefore more clearly distinguishable C_{60}^+ absorptions in Ne matrix have roughly the same linewidths of about 50 cm^{-1} . We assume that the absorption at 785 nm also has such a linewidth. With these assumptions, the quantum yield for the excitation at 785 nm is $\Phi_{785} \geq 4.2 \cdot 10^{-4}$. In a first approximation the quantum yield for other C_{60}^+ transitions in the ${}^2E_{1g} \leftarrow {}^2A_{1u}$ vibronic system is expected to be quite similar. Experimental data for other f_λ -numbers in neon and gas-phase cross-sections can be found elsewhere[9, 16].

Lifetime estimation

For the lifetime measurements, a Hamamatsu photomultiplier (R5509-43) was connected directly to the output of an optical fiber normally leading to the Raman spectrometer. The time resolution of the photomultiplier is about 2 ns, when using a $50 \text{ } \Omega$ input impedance. The laser signal was monitored with a Si photodiode. No significant difference between the time profile of the laser pulse and the LIF signal was observed, Fig. 5. Therefore the lifetime of the electronically excited state is less than 2 ns. Such a short lifetime is expected for the ${}^2A_{1u}$ state. from the linewidth observed for the allowed ${}^2A_{1u} \leftarrow {}^2E_{1g}$ electronic transition of C_{60}^+ , the gas-phase lifetime of the ${}^2A_{1u}$ state was estimated to be about 2 ps [5]. The matrix environment probably makes it even shorter. A similar lifetime (2.2 ± 0.2 ps) was found upon population of a vibronic state of the 2E_g electronically excited state of C_{60}^- by the fs-pump/probe photoelectron spectroscopy upon excitation at 775 nm [23]. We therefore also explored whether the first excited state of matrix isolated C_{60}^- (absorption maximum at 1066 nm in gas phase [24]) shows measurable fluorescence. In matrixes also containing fullerene anions we did not observe a LIF signal from C_{60}^- upon excitation of its near-IR

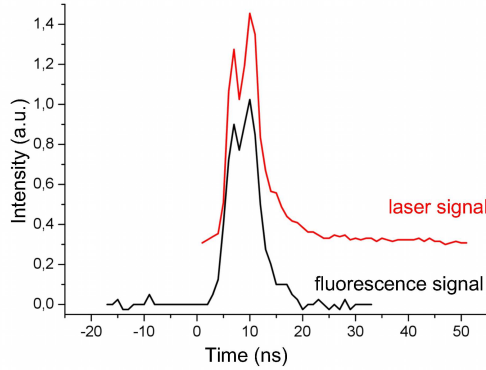


FIG. 5: Time dependence of the fluorescence signal versus that of the pulsed laser excitation source (923 nm). Note the strong similarity indicating that the fluorescence lifetime is than 2 ns.

vibronic bands.

Temperature dependence

Neon is not a convenient matrix within which to probe the temperature dependence of fluorescence processes, since Ne sublimates already at about 12 K. For such measurements we prepared a Kr matrix, containing C_{60}^+ . The absorption spectrum of C_{60}^+ in Kr differs somewhat from that in Ne, see Fig. 6a, but one can still measure pronounced LIF of C_{60}^+ , Fig. 6b. Increasing the matrix temperature influences the optical properties of the solid. At higher temperatures solid krypton scatters less than at lower temperatures. This can be seen by the scattering offset of the absorption spectra which is induced by changing temperature (Fig. 6a). Nevertheless, one does not observe a significant change of the LIF signal. For temperatures up to 45 K, the integrated emission intensity decreases by less than 7% (785 nm excitation). The spectra presented were obtained by depositing 8500 nAmin of C_{60}^+ at 5 K. Absorption and LIF measurements were done after annealing the matrix to 50 K (and subsequent cooling) to avoid possible changes of spectra due to diffusion of impurities or structural rearrangements of solid Kr.

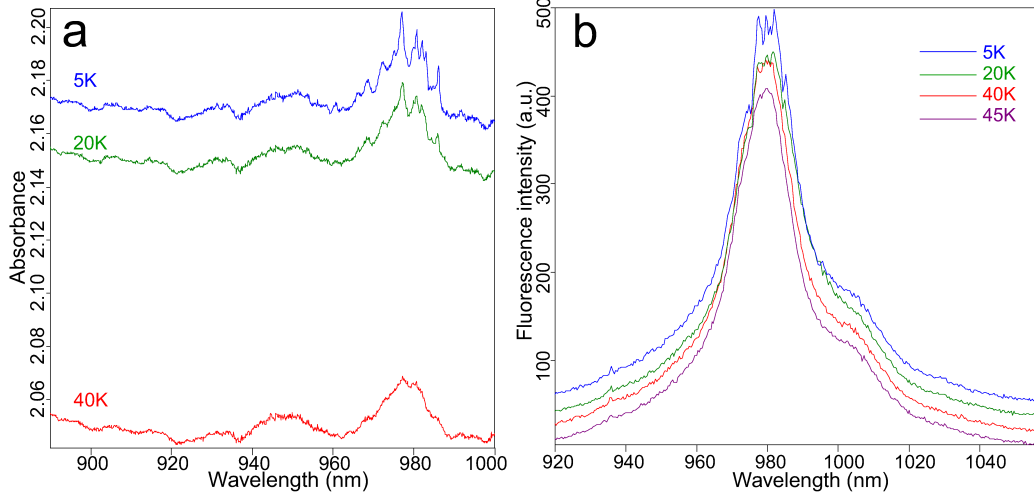


FIG. 6: **(a)** Absorption spectra of $C_{60}^{+/-/0}$ in Kr matrix at various temperatures. The offset is real and is caused by changes of the optical properties of solid krypton, which lead to increased light scattering as the sample is cooled below 40 K. **(b)** LIF spectra of $C_{60}^{+/-/0}$ in Kr matrix at various temperatures (785 nm excitation). Original spectra have a similar baseline. A vertical offset was added to better distinguish the individual spectra.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (KA 972/10-1). We also acknowledge support by KIT and Land Baden-Württemberg.

-
- [1] J. Cami, J. Bernard-Salas, E. Peeters, and S. Malek, *Science* **329**, 1180 (2010).
 - [2] D. García-Hernández, A. Manchado, P. García-Lario, L. Stanghellini, E. Villaver, R. Shaw, R. Szczerba, and J. Perea-Calderón, *Astrophys. J.* **724**, L39 (2010).
 - [3] K. Sellgren, M. W. Werner, J. G. Ingalls, J. D. T. Smith, T. M. Carleton, and C. Joblin, *Astrophys. J., Lett.* **722**, L54 (2010).
 - [4] M. Otsuka, F. Kemper, S. Hyung, B. A. Sargent, M. Meixner, A. Tajitsu, and K. Yanagisawa, *Astrophys. J.* **764**, 77 (2013).
 - [5] E. K. Campbell, M. Holz, D. Gerlich, and J. P. Maier, *Nature* **523**, 322 (2015).
 - [6] G. A. H. Walker, D. A. Bohlender, J. P. Maier, and E. K. Campbell, *Astrophys. J., Lett.* **812**, L8 (2015).

- [7] T. P. Snow and B. J. McCall, *Annu. Rev. Astron. Astrophys.* **44**, 367 (2006), <http://dx.doi.org/10.1146/annurev.astro.43.072103.150624>.
- [8] O. Berné, G. Mulas, and C. Joblin, *Astron. Astrophys.* **550**, L4 (2013).
- [9] Strelnikov, D., Kern, B., and Kappes, M. M., *Astron. Astrophys.* **584**, A55 (2015).
- [10] H. Van Winckel, M. Cohen, and T. R. Gull, *Astron. Astrophys.* **390**, 147 (2002).
- [11] “TURBOMOLE V6.4 2012, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>,”.
- [12] A. Sassara, G. Zerza, and M. Chergui, *J. Phys. B* **29**, 4997 (1996).
- [13] S. P. Sibley, S. M. Argentine, and A. H. Francis, *Chem. Phys. Lett.* **188**, 187 (1992).
- [14] K. Palewska, J. Sworakowski, H. Chojnacki, E. C. Meister, and U. P. Wild, *J. Phys. Chem.* **97**, 12167 (1993), <http://dx.doi.org/10.1021/j100149a011>.
- [15] J. Fulara, M. Jakobi, and J. Maier, *Chem. Phys. Lett.* **211**, 227 (1993).
- [16] E. K. Campbell, M. Holz, J. P. Maier, D. Gerlich, G. A. H. Walker, and D. Bohlender, *Astrophys. J.* **822**, 17 (2016).
- [17] P. Castellanos, O. Berné, Y. Sheffer, M. G. Wolfire, and A. G. Tielens, *Astrophys. J.* **794**, 83 (2014).
- [18] I. A. Simonia, *Astrophysics* **47**, 530 (2004).
- [19] B. Kern, D. Strelnikov, P. Weis, A. Böttcher, and M. M. Kappes, *J. Phys. Chem. A* **117**, 8251 (2013), <http://pubs.acs.org/doi/pdf/10.1021/jp4054605>.
- [20] B. Kern, D. Strelnikov, P. Weis, A. Böttcher, and M. M. Kappes, *J. Phys. Chem. Lett.* **5**, 457 (2014), PMID: 26276592, <http://dx.doi.org/10.1021/jz402630z>.
- [21] K. T. Schomacker, J. K. Delaney, and P. M. Champion, *J. Chem. Phys.* **85**, 4240 (1986), <http://dx.doi.org/10.1063/1.451795>.
- [22] R. C. Hilborn, *ArXiv Physics e-prints* (2002), physics/0202029.
- [23] O. T. Ehrler, J. P. Yang, C. Hättig, A.-N. Unterreiner, H. Hippler, and M. M. Kappes, *J. Chem. Phys.* **125**, 074312 (2006), <http://dx.doi.org/10.1063/1.2244557>.
- [24] S. Tomita, J. U. Andersen, E. Bonderup, P. Hvelplund, B. Liu, S. B. Nielsen, U. V. Pedersen, J. Rangama, K. Hansen, and O. Echt, *Phys. Rev. Lett.* **94**, 053002 (2005).

This figure "C60LIFGIMP1.png" is available in "png" format from:

<http://arxiv.org/ps/1704.01516v1>